

Supporting Information for

Si Microwire-Array Photocathodes Decorated with Cu Allow CO₂ Reduction with Minimal Parasitic Absorption of Sunlight

Paul A. Kempler¹, Matthias H. Richter¹, Wen-Hui Cheng²,
Bruce S. Brunschwig³, Nathan S. Lewis^{1,3*}

¹Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena,
CA 91125

²Division of Engineering and Applied Science, California Institute of Technology, Pasadena,
CA 91125

³Beckman Institute, California Institute of Technology, Pasadena, CA 91125

*Corresponding Author: nslewis@caltech.edu

This PDF file includes:

Equation S1

Figures S1 to S10

Tables S1 to S2

Detailed Materials and Experimental Methods

Materials: Isopropyl alcohol, acetone, hydrochloric acid (36.5 - 38.0 %), and nitric acid (67 - 70 %, TraceMetal Grade) were purchased from Millipore, and CuSO₄ was purchased from Flinn Scientific. Sulfuric Acid (TraceMetal Grade) was purchased from Fisher. Ammonium hydroxide (28 – 30 %) was purchased from JT Baker. K₂SO₄ (99 %), and potassium bicarbonate (99.995 %) were purchased from Sigma-Aldrich. Methanol was purchased from VWR Chemical and hydrogen peroxide (30 %) was purchased from Macron. Buffered oxide etchant (6:1 NH₄F/HF) was purchased from Transene.

Boron doped, P-type silicon wafers with a resistivity of 10 - 20 $\Omega\cdot\text{cm}$ were purchased from Addison Engineering. Platinum foil (99.99 %) was purchased from Alfa Aesar, and copper foil (99.999 %) was obtained from Sigma Aldrich. CO₂ (99.999 %, <1.0 ppm Ar+O₂+CO, <1.0 ppm THC, <3.0 ppm H₂O, <5.0 ppm N₂) was purchased from Airgas.

Preparation of Si Photocathodes: Si was degreased with acetone and isopropyl alcohol and was then spin coated at 4000 rpm for 30 s with Shipley 1813 photoresist. A square array of circles, having a diameter of 3 μm and a pitch of 7 μm , was defined using UV exposure through a chrome mask. The pattern was developed with MF-319 developer, and the resist was hard-baked at 115 °C for 10 min. Al₂O₃ masks, 125 nm in thickness, were deposited via e-beam evaporation at 1 $\text{\AA}\cdot\text{s}^{-1}$ into the exposed hole array and the resist was removed via sonication in Remover-PG (MicroChem) at 50 °C. Si was structured into 30 μm tall microwire arrays via deep reactive ion etching (RIE) in a SF₆/O₂ plasma controlled by an Oxford Plasmalab System 100 at -130 °C. An inductively coupled plasma power of 900 W produced etching rates of 1 $\mu\text{m min}^{-1}$, while a low capacitively coupled plasma power of 3 W minimized sidewall damage and mask removal. All Si samples were cleaned in a Radio Corporation of America, RCA, SC1 bath (5:1:1

H₂O/NH₄OH/H₂O₂, 80 °C for >10 min), buffered oxide etchant (20 °C for 5 min), and an RCA SC2 bath (6:1:1 H₂O/HCl/H₂O₂, 70 °C for >10 min) to remove SiO₂, Al₂O₃ and trace metal impurities. A solid-state n⁺p junction was formed via diffusion doping from CeP₂O₁₄ doping wafers (Saint-Gobain, PH-900 PDS) at 850 °C for 10 min. The P₂O₅ glass formed during the doping procedure was removed from the Si surface via buffered oxide etchant for > 60 s prior to electrodeposition. Samples were cleaved with a carbide scribe into ~10 mm² chips. Ga/In eutectic was scratched into the back of the electrodes, and the electrodes were attached to a Sn-coated Cu wire using Ag paint (Ted Pella). The back contact and sides of the electrodes were sealed to 6 mm outer diameter glass tubing using insulating epoxy (Loctite 9460). The epoxy was cured for at least 12 h. The area of the electrodes was measured with a commercial scanner.

(Photo)electrodepositions of Catalyst: Prior to electrodeposition of Cu, electrodes were rinsed sequentially with acetone, isopropyl alcohol, methanol, and deionized water and then dipped into buffered oxide etchant for 60 s. Electrodepositions were controlled with a BioLogic SP-200 potentiostat. The Cu-plating bath was continuously purged with Ar(g) and contained 0.10 M CuSO₄(aq), 5.0 mM H₂SO₄(aq), and 0.10 M K₂SO₄(aq), at a pH of ~3. A saturated calomel electrode (SCE, CH Instruments) was used as a reference and the counter electrode was a high-purity graphite rod (Alfa Aesar, 5N) (**Figure 1a**). The illumination source was an array of narrowband light-emitting diodes (Luxeon Rebel Blue SMD, FWHM 22 nm) with a peak intensity at 465 nm. The illumination wavelength was selected to maximize transmission of light through the colored electrolyte. Cu was deposited potentiostatically at 0.0 V vs. SCE until the desired charge density had passed, normalized to the projected area of the electrode.

Photoelectrochemical CO₂ Reduction Testing: The electrochemical setup was operated in a continuous flow mode (**Figure S1**). Carbon dioxide was provided to the electrochemical cell at a

flow rate of 5 sccm as controlled by an Alicat flow controller. The carbon dioxide stream was supplied as humidified CO₂ with a gas bubbler placed between the cell and flow controller. The exhaust gases went through a liquid trap, then an Alicat flow meter, and finally to a gas chromatograph (SRI-8610) using a Hayesep D column and a Molsieve 5A column with N₂ as the carrier gas. The gaseous products were detected using a thermal conductivity detector (TCD) and a flame ionization detector (FID) equipped with a methanizer. Quantitative analysis of gaseous products was based on calibrations with several gas standards over many orders of magnitude in concentration. The calibrations were used to calculate the partial current density, j , towards products of the CO₂R and hydrogen evolution reaction. To measure liquid products, the electrolyte on the anode and cathode sides of the cell was sampled at the end of the run and was analyzed by high-performance liquid chromatography (HPLC, Thermo Scientific Ultimate 3000). Products were not quantified in Faradaic efficiency calculations because continuous purging of the catholyte with CO₂ expelled accumulated products. Moreover, crossover of products to the anolyte was observed and oxidation at the anode could potentially occur. An Oriel Instruments 75 W Solar Simulator supplied 100 mW·cm⁻² of AM 1.5 illumination. The light intensity was calibrated using the measured photocurrent at a calibrated (350 to 1100 nm, 1 cm²) NIST traceable Si photodiode (Thorlabs FDS1010-CAL) mounted within the testing cell prior to the addition of the electrolyte.

Electrochemical measurements of GDE cell: A PEEK compression cell (**Figure S1**) was used as the vessel for the measurement with an anode chamber volume of 2 mL and a cathode chamber volume of 4 mL. The anode, cathode electrode and membrane area were each 1 cm² as constrained by the design of the compression cell. CO₂ saturated 0.10 M potassium bicarbonate (KHCO₃, pH 6.8) was used as the electrolyte. A Pt foil anode was used behind a Selemion anion

exchange membrane. A leakless Ag/AgCl electrode was used as a reference. All electrochemical measurements were performed using a Biologic VSP-300 potentiostat. Scan rates were set to 50 mV·s⁻¹. Cu foil (99.999 %, Sigma Aldrich) was mechanically polished (Struers LabPol-5) using 0.050 µm alumina suspension (MasterPrep) and then was electropolished for 5 min in 85% H₃PO₄ at +2.1 V vs. a carbon counter electrode.

Physical Characterization: Scanning-electron micrographs (SEMs) were obtained with a FEI Nova NanoSEM 450 at an accelerating voltage of 10.0 kV and a working distance of 5.0 mm using an Everhart-Thornley secondary electron detector.

Comparison of Catalyst Loadings: The mass loadings of catalyst were compared assuming a Faradaic efficiency of ~100 % towards metal plating. Equation S1 can be used to calculate the mass loading density, M_{cat} (mg·cm⁻²), from the cathodic charge density, $-Q$ (C·cm⁻²) and molar mass of the catalyst. For Cu ($m_a = 63.55$ g·cm⁻²), M_{cat} was 0.329 and 0.0487 mg·cm⁻² for $-Q = 1$ and 0.148 C·cm⁻², respectively.

$$M_{cat} = \frac{-Qm_a}{nF} \quad (S1)$$

Explanation of Resistance Measurement and iR_s Correction: The resistance (R_s) was determined by electrochemical impedance spectroscopy (EIS) at the open-circuit potential. During the experiment, iR_s was corrected by 85% and the remaining 15 % was corrected for after the experiment.

Measurements of Pt Crossover during Stability Testing The rate of Pt dissolution in 0.10 M KHCO₃(aq) and crossover through Selemion were measured via a galvanostatic experiment at 10 mA using a Pt anode and a graphite cathode. The volumes of the anolyte and catholyte were each

13 mL. ICP-MS measurements confirmed the presence of dissolved Pt in both the anolyte and catholyte (**Table S2**).

Predicted j - E behavior: Illuminated j - E behavior was predicted by shifting the fitted Tafel behavior of the polished Cu foil towards positive potentials by $V_{ph} + b \log_{10}(R_{\mu})$. This calculation assumes a comparable microstructured area of Cu islands and Si and similar $[H^+(aq)]$ and $[CO_2(aq)]$ at the surface of the two electrodes. Simulated j - E behaviors in Figure 4b were produced by summing the implicit values for η and V_{ph} , calculated from Equations 1 and 2, as a function of R_{μ} and b . Arbitrary values were selected for $J_o = 1 \times 10^{-10} \text{ A cm}^{-2}$ and $a = b \log_{10}(i_0)$, with $i_0 = 1 \times 10^{-7} \text{ A cm}^{-2}$; these parameters do not affect the potential shift resulting from a change in R_{μ} but affect the total V_{ph} and η observed.

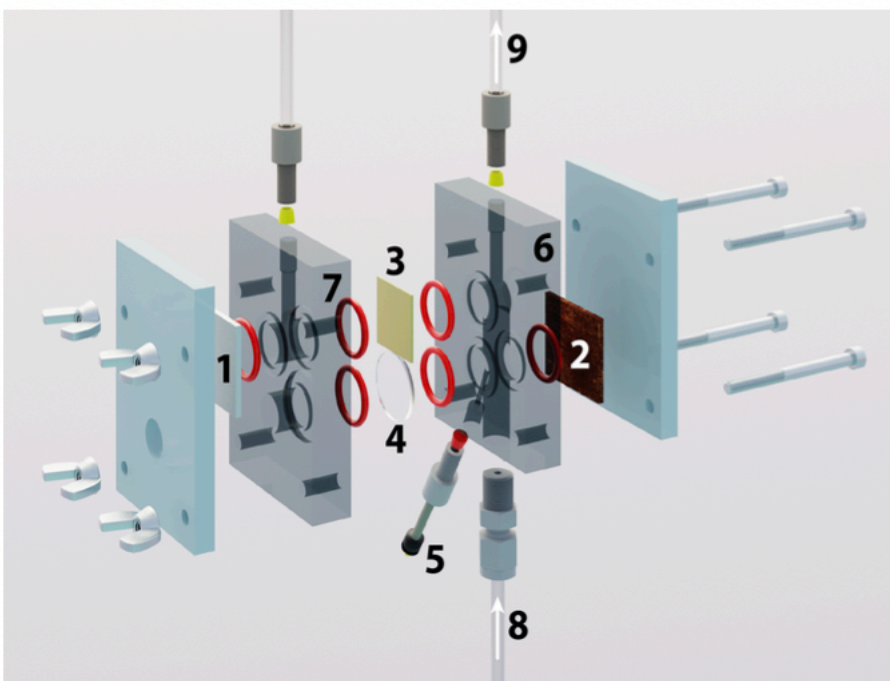


Figure S1: Cell configuration composed of 1 Pt anode, 2 Si μ W cathode, 3 anion exchange membrane, 4 quartz window, 5 reference electrode, 6 catholyte chamber, 7 anolyte chamber, 8 CO_2 gas inlet, and 9 product/ CO_2 outlet. Illumination to the cathode is provided through a hole in the left side of the compression cell, which extends through the anolyte chamber plate and the quartz window (4) to the μ Si μ W cathode.

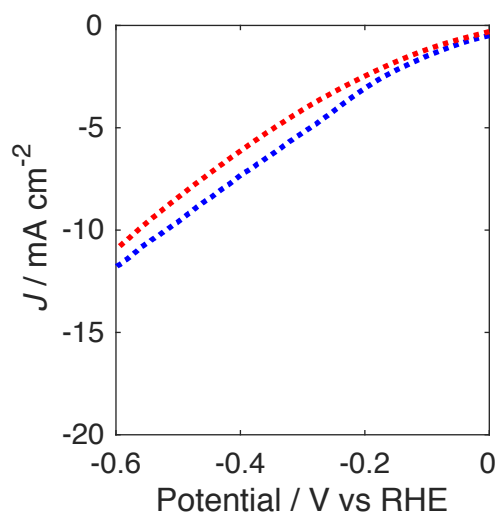


Figure S2: Electrochemical J - E behavior of polished graphite (dotted lines) in an Ar purged Cu deposition bath, before (blue) and after (red) passage of a charge density of $-1.00 \text{ C}\cdot\text{cm}^{-2}$.

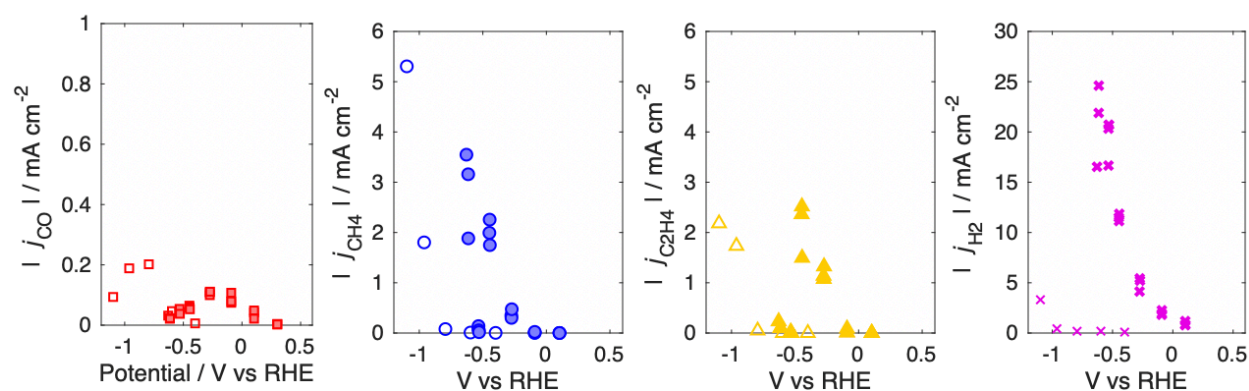


Figure S3: Plots of the partial current densities towards (photo)electrochemical CO_2R products vs. potential for $n^+\text{p-Si } \mu\text{W/Cu}$ electrodes (filled markers) compared to planar Cu electrodes (open markers). (a) $j_{\text{CO}}\text{-}E$ behavior for production of CO, (b) $j_{\text{CH}_4}\text{-}E$ behavior for production of CH_4 , (c) $j_{\text{C}_2\text{H}_4}\text{-}E$ behavior for production of C_2H_4 , and (d) $j_{\text{H}_2}\text{-}E$ behavior for production of H_2 , detected by online GC-FID/TCD.

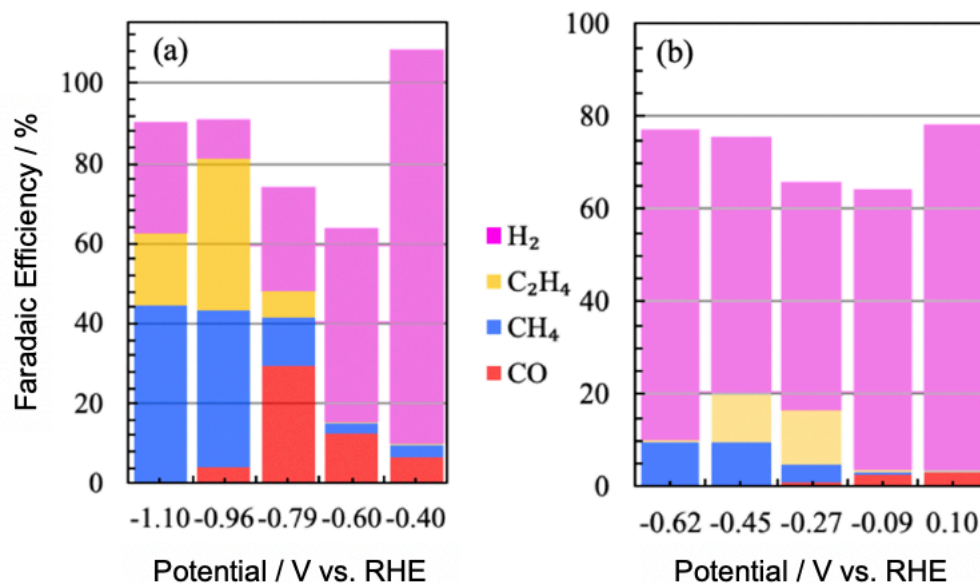


Figure S4: Faradaic efficiencies for products detected via GC-FID/TCD, as a function of potential during CO₂R in 0.10 M KHCO₃(aq) saturated with CO₂(g) at: (a) an electropolished Cu film, and (b) a n⁺p-Si μW/Cu photocathode under simulated sunlight.

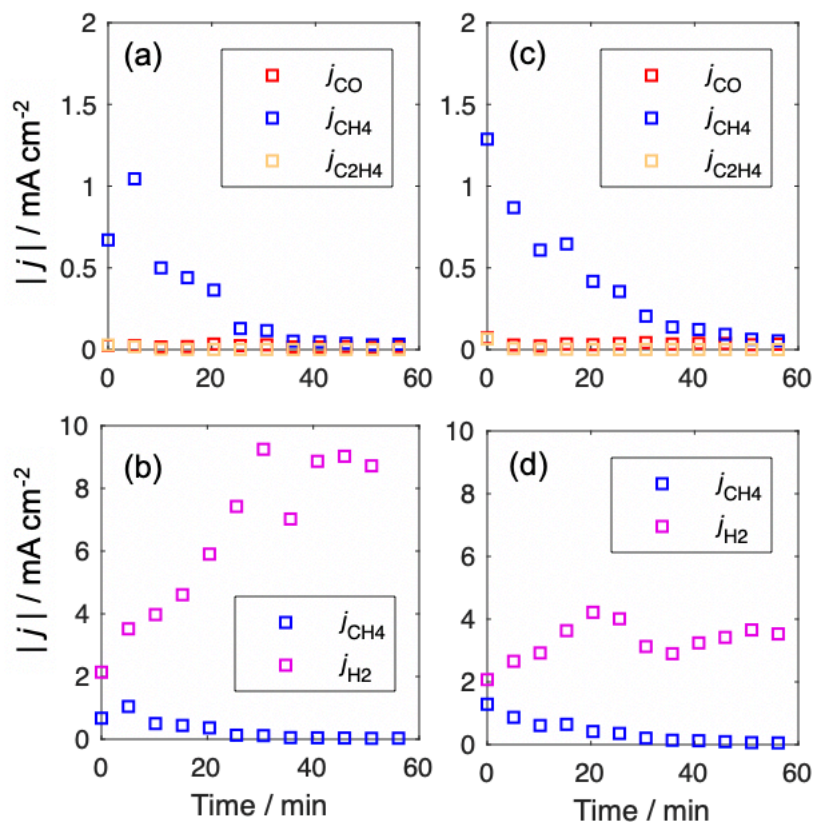


Figure S5: Partial photocurrent density towards CH₄, C₂H₄, CO, and H₂, respectively, as measured via GC-FID/TCD, represented as blue, gold, red, and magenta squares, respectively. Planar n⁺p-Si after (a,b) -1.00 C cm⁻² or (c,d) -0.148 C cm⁻² of charge was passed towards Cu deposition. Electrodes were held under simulated sunlight at -0.69 V vs RHE in 0.10 M KHCO₃(aq) saturated with CO₂(g).

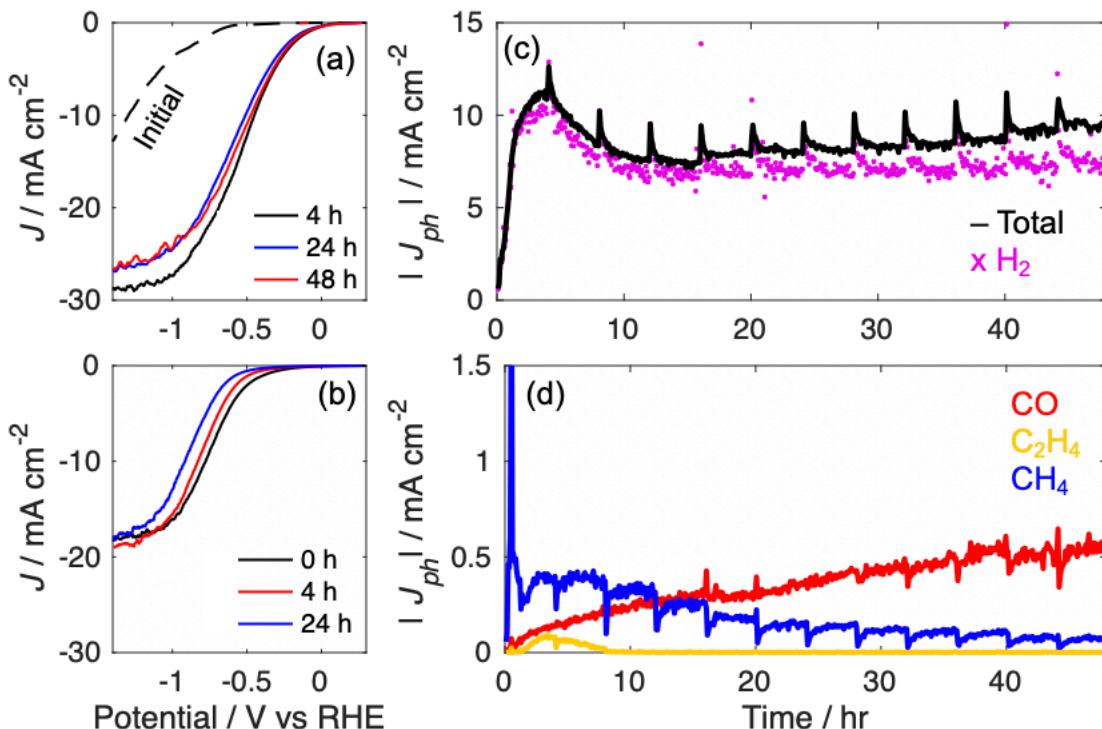


Figure S6: Photoelectrochemical data for n⁺p-Si Cu electrodes during stability evaluation at -0.58 V vs. RHE in CO₂-purged 0.10 M KHCO₃(aq) under 100 mW·cm⁻² simulated sunlight. (a-b) Time dependent J - E behavior for a (a) n⁺p-Si μ W/Cu electrode and (b) planar n⁺p-Si/Cu electrode, loaded with -1.00 and -0.148 C cm⁻², respectively, as measured by a linear sweep voltammogram recorded at a scan rate of 50 mV·s⁻¹. (c) Absolute photocurrent density and partial photocurrent density towards H₂(g), as measured via GC-FID/TCD, represented as black x's and a gray line, respectively for a n⁺p-Si μ W/Cu electrode. (d) Absolute partial photocurrent density towards CO(g), C₂H₄(g), and CH₄(g) presented as red, gold, and blue lines, respectively for a n⁺p-Si μ W/Cu electrode.

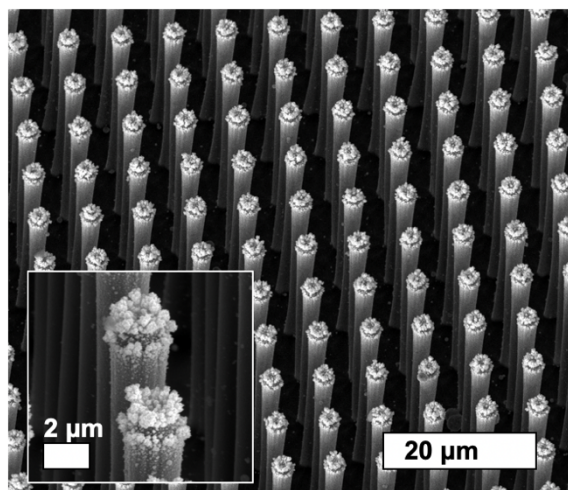


Figure S7: SEM of an n^+p -Si- μ W/Cu photocathode after 96 h of continuous photoelectrochemical operation in CO_2 -purged 0.10 M $\text{KHCO}_3(\text{aq})$ under $100 \text{ mW}\cdot\text{cm}^{-2}$ of simulated sunlight. Primary scale bar represents $20 \mu\text{m}$, inset scale bar represents $2 \mu\text{m}$.

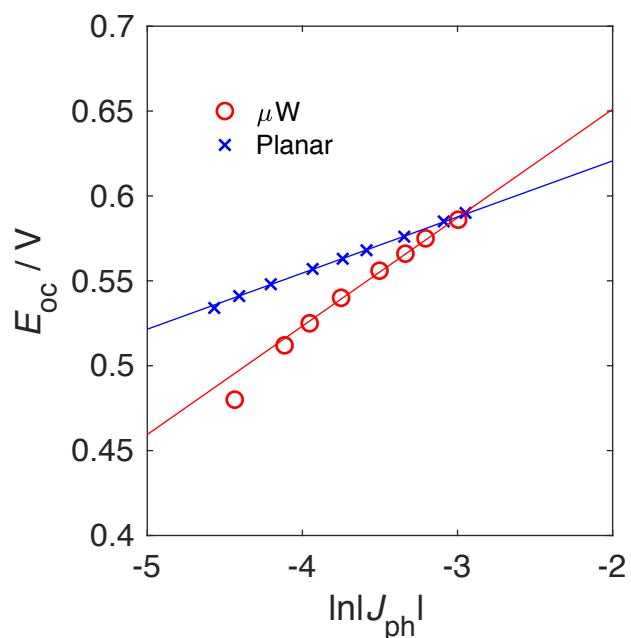


Figure S8: Plot of E_{oc} vs. the \ln of the light-limited photocurrent density ($\text{A}\cdot\text{cm}^{-2}$) in a Cu plating bath for planar and μW n^+p -Si. The illumination source was a narrow band LED with a peak intensity at 630 nm. The illumination wavelength was selected to maximize transmission through the Cu film. The ideality factor was calculated from the slope of the linear fit in range of photocurrent densities relevant to operation under $100 \text{ mW}\cdot\text{cm}^{-2}$ of simulated sunlight.

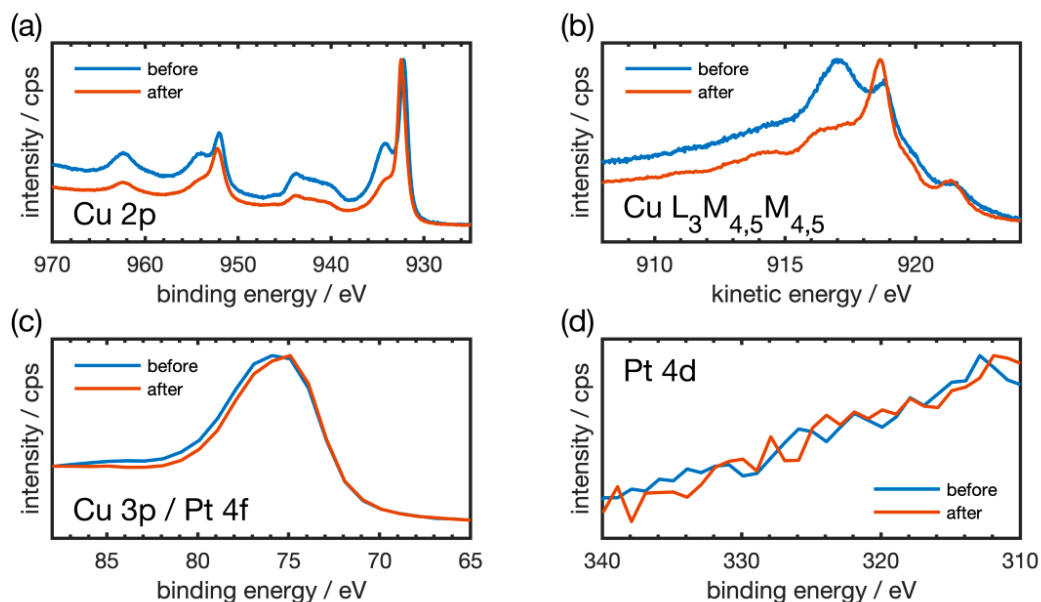


Figure S9: Surface characterization of films of sputtered Cu before and after sequential potential holds for 2 hr at -1.2, -1.0, -0.8, -0.6, and -0.4 V vs RHE in CO₂ saturated 0.10 M KHCO₃(aq). XPS spectra of (a) the Cu 2p region, (c) the Cu 3p and Pt 4f regions, (d) the Pt 4d region, and (b) Auger electron spectra in the Cu LMM region did not detect Pt on the surface but confirmed that Cu oxide species were reduced during testing.

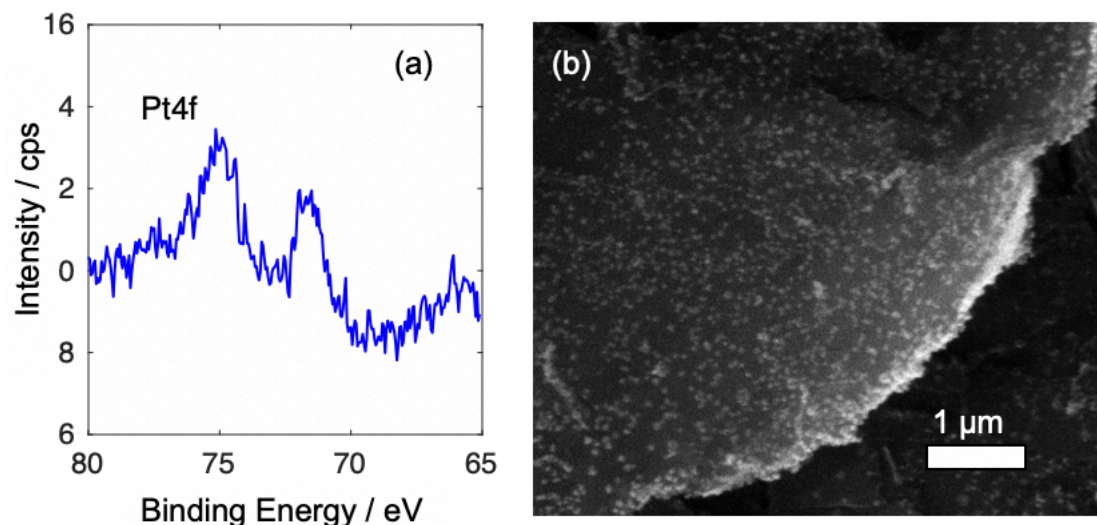


Figure S10: (a) X-ray photoelectron spectra of the surface of a graphite cathode in the Pt 4f region after 5 days under galvanostatic control at -10 mA in 0.10 M $\text{KHCO}_3(\text{aq})$. The graphite cathode was separated from a Pt anode by a Selemion membrane. (b) SEM image of the surface of the graphite surface measured in (a). Small metal nanoparticles, visible as white dots, were not present prior to the galvanostatic experiment.

Table S1: Liquid CO_2R products for a $\text{n}^+\text{p-Si } \mu\text{W/Cu}$ electrode after a 48 h stability test under $100 \text{ mW}\cdot\text{cm}^{-2}$ of simulated sunlight at -0.58 V vs. RHE in CO_2 -purged 0.10 M $\text{KHCO}_3(\text{aq})$. Dashes indicate measurements below the limit of quantitation.

Product	C_{cathode} (mM)	C_{anode} (mM)
Formate	13.5	7.9
Acetate	0.2	0.3
Methanol	-	-
Ethanol	0.3	3.4
Propanol	0.1	0.1
Allyl Alcohol	-	-
Ethylene Glycol	-	-

Table S2: Dissolved Pt concentration in the anolyte and catholyte, measured via inductively-coupled plasma mass-spectrometry, following a 5 day experiment with a constant current of 10 mA applied between a Pt foil anode and graphite cathode separated by Selemion AMV membrane.

	Pt [ug/L]	Pt error [ug/L]	Pt [ug]	Pt error [ug]
Anolyte	540	53	7.0	0.7
Catholyte	60	20	0.8	0.3